SHORT COMMUNICATION

Air Oxidation of Aqueous Cyanides in a Countercurrent Fixed Bed Reactor

Ahmet Alicilar*†, Melih Kömürcü and Atilla Murathan

Gazi University, Faculty of Engineering and Architecture, Chemical Engineering Department,
Maltepe, 06570, Ankara, Turkey

Abstract−This study was conducted to discuss the removal of cyanides from water by air oxidation. Experiments were carried out in a countercurrent fixed bed reactor for three different values of temperature, concentration, gas and liquid flow rates. It was operated at pH 12 by using delrin (formaldehyde polymer) as packing material. Effects of some operating parameters on the conversion were studied, and it was observed that the conversion percent increased by increasing temperature and decreasing gas and liquid flow rates. Effect of concentration was not steady. A conversion of 89% was achieved under optimum conditions while it ranges from 44 to 79% at room temperature.

Key words: Cyanide, Oxidation, Fixed Bed Reactor, Water Pollution

INTRODUCTION

Cyanides are useful materials industrially that have been employed for years in fields such as electroplating of metals, gold recovery from ores, treatment of sulfide ore slurries in flotation, etc. [Borbely et al., 1985]. Cyanide in aquatic environments comes not only from discharge of industrial effluent, but can also be of natural origin. Many plants, microbes and some insects are capable of releasing HCN upon enzymatic hydrolysis of certain compounds they produce [Basheer et al., 1993].

The toxicity of cyanides is well known, and liquid effluent from plants employing cyanides industrially has to be effectively controlled. A large number of studies have been done on the treatment of cyanide wastes. The common methods to treat it have always been chemical, namely to add certain oxidants such as chlorine or hypochlorite to decompose it. Methods used typically for the treatment of cyanide wastes are alkaline chlorination, electrolytic oxidation, ozonation, wet air oxidation and ion exchange [Gaudy et al., 1982; Gurol and Bremen, 1985; Walsht and Wilson, 1986; Ho et al., 1990; Kim et al., 1999].

The treatment processes are mainly based on oxidation, with two of the main methods being alkaline chlorination and hydrogen peroxide oxidation. Alkaline chlorination is highly penalizing in terms of reagent consumption. Hydrogen peroxide is selective for cyanide in solutions, but is an extremely expensive reagent [Devuyst et al., 1991]. As shown in the following reactions, cyanides can be converted to carbon dioxide and nitrogen by catalytic oxidation while the cyanate is obtained in mild conditions.

$$CN^- + OCl^- \rightarrow CNO^- + Cl^-$$
$$2CN^- + 2O_2 \rightarrow 2CO_2 + N_2$$
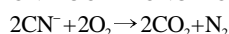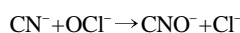
Also in recent years, numerous studies on oxidation of cyanides have been performed [Matatov and Sheintuch, 1998; Sharma et al., 1998; Alam and Kamath, 1998]. Fixed-bed reactors are one of the systems preferred in this type of reaction [Park et al., 2000; Horow-

itz et al., 2001; Pamuk et al., 2001]. The reason for the preference is their advantages such as effective particle wetting, reaching high conversion in a single reactor and ease of temperature control [Alicilar et al., 1994].

Some of the oxidative works have disadvantages such as high cost, harmful residue, and potential hazard in handling of oxidant reagent. This study was undertaken in an attempt to discuss the use of countercurrent fixed bed reactors for oxidation of aqueous cyanides. Air was used as oxidant and effects of some operating parameters on conversion were investigated.

MATERIALS AND METHODS

Fresh stock solutions were prepared by using potassium cyanide and double distilled water before each experiment. All chemicals used were of analytical reagent grade. The initial pH of the solution was adjusted to 12 by adding the saturated solution of potassium hydroxide. A pyrex-glass reactor having an inner diameter of 5.6 cm and a height of 64 cm was used in the experiments. Liquid feed was given to the column at the top while gas stream was fed to the bottom of the column. A distributor was placed at the column inlet in order to provide good distribution of the liquid phase. Air and potassium cyanide solution were utilized as gas and liquid phases, respectively. Cylindrical delrin particles (formaldehyde polymer) were used as packing material. The experimental set-up used in this study is given in Fig. 1 and the experimental conditions in Table 1.

Before each experiment was started, the column was drained by using distilled water until cyanide ions were not observed at the column outlet. Flow rates of the cyanide solution and air were kept constant during the experiments. The flows were measured with precalibrated rotameters. The jacket temperature was maintained at a constant value by means of circulating water from a thermostated water bath through the jacket surrounding the column. Three different values of jacket temperature, cyanide concentration, gas and liquid flow rates were studied in experiments [Kömürcü, 1999].

After the system reached steady state, liquid samples were collected from the column outlet and their cyanide concentration was determined by titration with $AgNO_3$ solution. The conversion per-

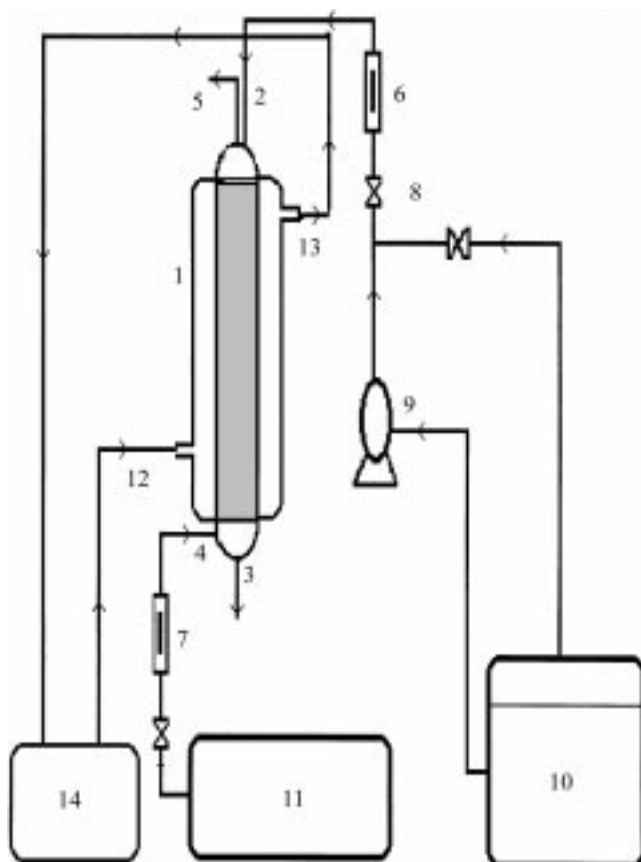†To whom correspondence should be addressed.
E-mail: alicilar@gazi.edu.tr

Fig. 1. Schematic diagram of the experimental set up.

1. Packed column	8. Valve
2. Liquid inlet	9. Peristaltic pump
3. Liquid outlet	10. Liquid tank
4. Gas inlet	11. Compressor
5. Gas outlet	12. Heating water inlet
6. Liquid rotameter	13. Heating water outlet
7. Gas rotameter	14. Thermostated bath

Table 1. Experimental conditions

Column diameter (cm)	5.6
Bed height (cm)	64
Diameter of packing material (mm)	5
Height of packing material (mm)	5
Cyanide concentrations in solutions (M)	0.005, 0.04, 0.1
Liquid flow rates (L/min)	1.5, 3, 4.5
Gas flow rates (L/min)	0.3, 0.6, 0.9
Temperatures of heating water (^{o}C)	18, 45, 60
pH	12

cent was calculated from the difference between these concentration values and the initial ones.

RESULTS AND DISCUSSION

This study was only performed in basic medium because gaseous HCN is formed under acidic conditions. Effects of several parameters such as liquid and gas flow rates, temperature, initial concentration on conversion were investigated. Typical results of ex-

periments obtained in order to determine the effects of liquid flow rate on the conversion are given in Fig. 2. As seen from the figure, an increase in liquid flow rate results in decrease of the conversion percent. This decrease is more clearly seen at the low values of con-
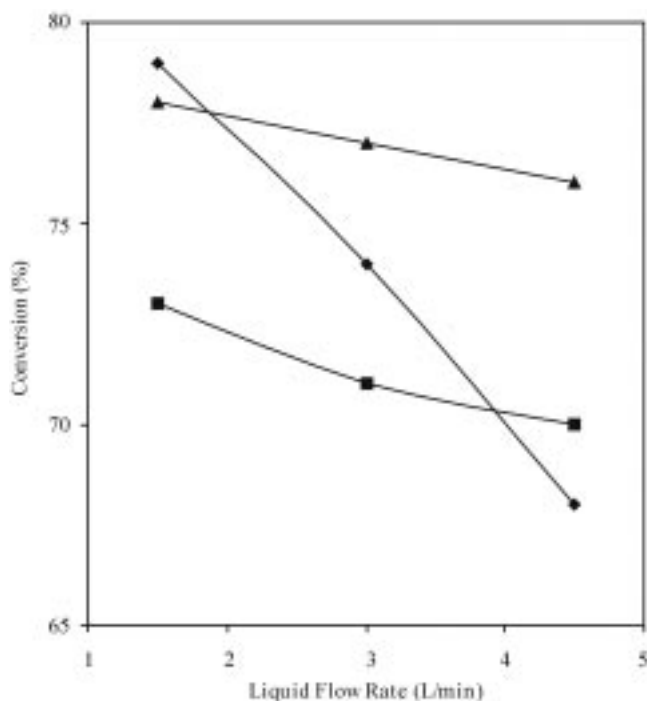

Fig. 2. Effects of liquid flow rate on conversion (◆ C_o=0.005 M, T=18 ^{o}C, u_G=0.3 L/min ■ C_o=0.04 M, T=45 ^{o}C, u_G=0.6 L/min ▲ C_o=0.1 M, T=60 ^{o}C, u_G=0.9 L/min).
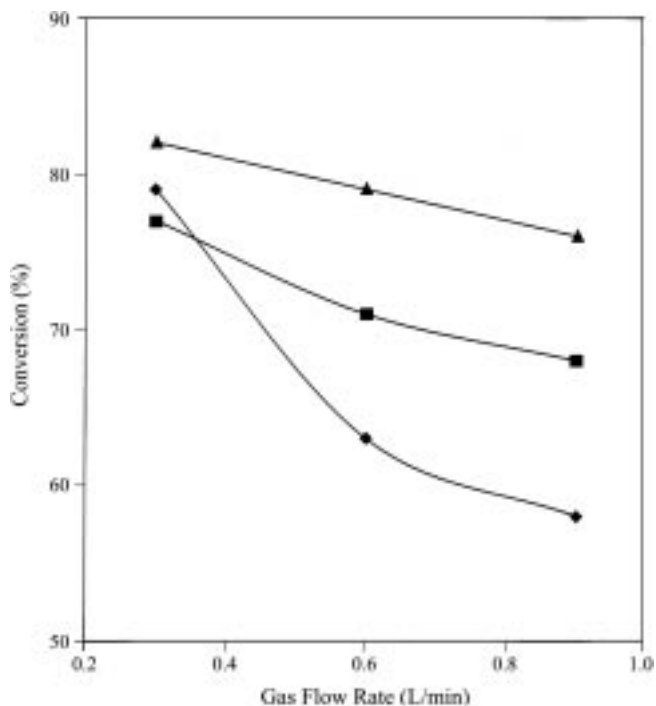
Fig. 3. Effects of gas flow rate on conversion (◆ C_o=0.005 M, T=18 ^{o}C, u_L=1.5 L/min ■ C_o=0.04 M, T=45 ^{o}C, u_L=3 L/min ▲ C_o=0.1 M, T=60 ^{o}C, u_L=4.5 L/min).

centration, temperature and gas flow rate. This change in the conversion percent is attributable to the decrease of contact time between the reactants due to the increase in liquid flow rate.

The change of conversion percent depending on the gas flow rate is shown in Fig. 3. The effect of gas flow rate on the conversion is similar to that of the liquid. The conversion percent decreases with increasing the gas flow rate. However, this decrease cannot be explained by the decrease in contact time as in the case of different liquid flow rates. The conversion percent was calculated based on the amount of cyanides remained in water and, the gas flow rate was not taken into account for these calculations. Therefore, the effect of gas flow should be explained with other factors.

It may be argued that the higher gas flow decreases the temperature of the bed and the conversion. This cooling effect of gas flow may be confirmed by the results obtained for the jacket temperature (Fig. 4). At especially high temperatures, this effect is important in experiments. However, similar results obtained at room temperature cannot be explained in this way. The mass transfer effects should be taken into account in this case.

Under these conditions, the decrease in conversion depending on the increase in gas flow rate probably results from the decrease in contacting efficiency between gas and liquid phases. The resistance to flow is lower near the wall where the voidage is higher than that in the center of the column [Xiao, 2001]. When the gas flow rate is increased, the gas phase prefers to flow near the wall. As a result, by-pass increases due to the formation of channelling, especially as wall flow, in the bed and the contact between gas and liquid phases decreases. This case results in a decrease in the conversion percent.

The effect of jacket temperature on the conversion is represented in Fig. 4. The reaction accelerates by increasing temperature. In addition to this, the contacting efficiency between the reactants in-
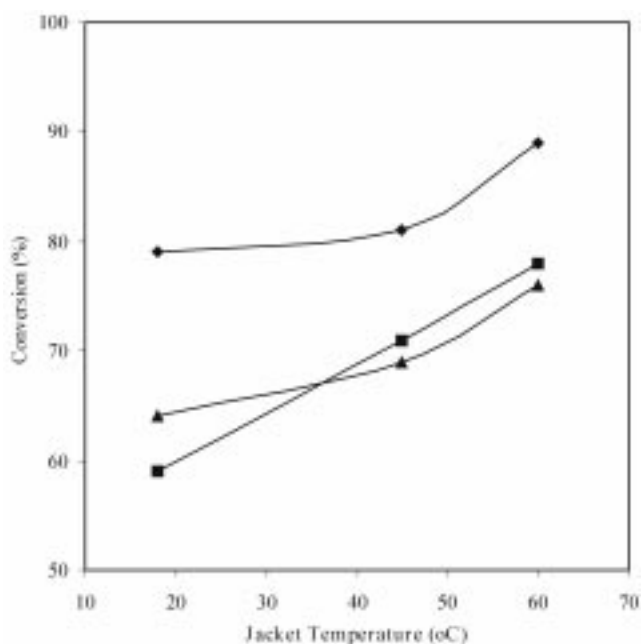

Fig. 5. Effects of concentration on conversion at room temperature ($\blacklozenge$ u_G=0.3 L/min, u_L=1.5 L/min $\blacksquare$ u_G=0.6 L/min, u_L= 3 L/min $\blacktriangle$ u_G=0.9 L/min, u_L=4.5 L/min).

creases because ionic mobility increases as a result of increase in temperature. By depending on these effects, the conversion percent increases with an increase in temperature as expected [Pak and Chang, 1997].

Change of the conversion percent as a function of the initial concentration is shown in Fig. 5. It has been only drawn for room temperature because similar behaviour was observed at high temperatures too. As seen from the figure, the conversion continuously increased with increasing concentration in some cases. However, it was mostly decreased at the beginning and then increased. The continuous increase may be admitted as a usual result, but not the other one. The decrease plus increase is probably arisen from the change of contacting efficiency between the reactants by depending on flow properties in the column [Alicilar et al., 1994].

CONCLUSION

Techniques for the treatment of cyanides are mainly based on oxidation. Oxidants and catalysts used for this purpose are usually high cost materials. This work was performed under the liquid down- and gas up-flow conditions in a fixed bed reactor. Air was used as an oxidant. Although it was worked as a continuously operating system, a conversion of 89% was attained at the optimum conditions comprising a water temperature of 60 °C, a gas flow rate of 0.3 L/min and liquid flow rate of 1.5 L/min. The conversion observed at room temperature was also quite high (79%).

Fig. 4. Effects of temperature on conversion ($\blacklozenge$ C_o=0.005 M, u_G= 0.3 L/min, u_L=1.5 L/min $\blacksquare$ C_o=0.04 M, u_G=0.6 L/min, u_L= 3 L/min $\blacktriangle$ C_o=0.1 M, u_G=0.9 L/min, u_L=4.5 L/min).

NOMENCLATURE

C_o : initial concentration [M]
T : jacket temperature [°C]
u_G : gas flow rate [L/min]

u$_L$: liquid flow rate [L/min]

REFERENCES

Alam, M. and Kamath, S., "Cyanide Destruction in Molten Carbonate Bath: Melt and Gas Analyses," *Env. Sci. Tech.*, **32**(24), 3986 (1998).

Alicilar, A., Bicer, A. and Murathan, A., "The Relation Between Wetting Efficiency and Liquid Holdup in Packed Columns," *Chem. Eng. Comm.*, **128**, 95 (1994).

Basheer, S., Kut, Ö. M., Prenosil, J. E. and Bourne, J. R., "Development of an Enzyme Membrane Reactor for Treatment of Cyanide-Containing Wastewaters from the Food Industry," *Biotech. Bioeng.*, **41**, 465 (1993).

Borbely, G. J., Cliff, C., Devuyst, E. A., Ettel, V. A., Mosoiu, M. A. and Schitka, K. J., US Patent 4, 537686 (1985).

Devuyst, E. A., Robbins, G., Vergunst, R., Tandi, B. and Iamarino, P. F., "Inco's Cyanide Removal Technology Working Well," *Mining Eng.*, **2**, 205 (1991).

Gaudy, A. F., Gaudy, Jr. E. T., Feng, Y. J. and Brueggemann, Y. G., "Treatment of Cyanide Waste by the Extended Aeration Process," *JWPCF*, **54**(2), 153 (1982).

Gurol, M. D. and Bremen, W. M., "Kinetics and Mechanism of Ozonation of Free Cyanide Species in Water," *Env. Sci. Tech.*, **19**(9), 804 (1985).

Ho, S. P., Wang, Y. Y. and Wan, C. C., "Electrolytic Decomposition of Cyanide Effluent with an Electrochemical Reactor Packed with Stainless Steel Fibre," *Wat. Res.*, **24**(11), 1317 (1990).

Horowitz, G. I., Martinez, O., Cukierman, A. L. and Cassanello, M. C., "Ethanol Oxidation in a Trickle Bed Reactor using a Hydrophobic Catalyst Effect of Dilution with Hydrophilic Particles," *Catal. Today*, **64**(3-4), 347 (2001).

Kim, S. J., Hwang, K. R., Cho, S. Y. and Moon, H., "Simultaneous Removal of Cyanide and Copper Ions in a Semi-fluidized Ion Exchanger Bed," *Korean J. Chem. Eng.*, **16**, 664 (1999).

Kömürcü, M., "Oxidation of Cyanide in Water in Packed Column," M.S. Thesis, Gazi University, Ankara, Turkey (1999).

Matatov, M. Y. and Sheintuch, M., "Catalytic Abatement of Water Pollutants," *Ind. Eng. Chem. Res.*, **37**(2), 309 (1998).

Pak, D. and Chang, W., "Oxidation of Aqueous Cyanide Solution using Hydrogen Peroxide in the Presence of Heterogeneous Catalyst," *Env. Tech.*, **18**(5), 557 (1997).

Pamuk, V., Yilmaz, M. and Alicilar, A., "The Preparation of D-Glucaric Acid by Oxidation of Molasses in Packed Beds," *J. Chem. Tech. Biotech.*, **76**(2), 186 (2001).

Park, Y. H., Kim, S. J. and Kang, S. C., "Effect of the Reaction Bath Temperature in a Fixed-Bed Reactor for Oxidation of o-Xylene over V$_2$O$_5$/TiO$_2$ Catalysts," *Korean J. Chem. Eng.*, **17**, 81 (2000).

Sharma, V. K., Rivera, W., Smith, J. D. and Brandon, B., "Ferrate (IV) Oxidation of Aqueous Cyanide," *Env. Sci. Tech.*, **32**(17), 2608 (1998).

Walsht, F. and Wilson, G., "The Electrolytic Removal of Gold from Spent Electroplating Liquors," *Trans. IMF*, **64**, 55 (1986).

Xiao, Q., Cheng, Z. M., Jiang, Z. X., Anter, A. M. and Yuan, W. K., "Hydrodynamic Behavior of a Trickle Bed Reactor Under Forced Pulsing Flow," *Chem. Eng. Sci.*, **56**, 1189 (2001).